Applied Thermal Engineering 66 (2014) 15–24

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

A review of thermoelectric cooling: Materials, modeling and applications

Dongliang Zhao, Gang Tan*

University of Wyoming, Department of Civil and Architectural Engineering, 1000 E. University Avenue, Dept. 3295, Laramie, WY 82071, USA

HIGHLIGHTS

- Thermoelectric cooling has great prospects with thermoelectric material's advances.
- Modeling techniques for both thermoelement and TEC have been reviewed.
- Principle thermoelectric cooling applications have been reviewed and summarized.

ARTICLE INFO

Article history:
Received 5 December 2013
Accepted 31 January 2014
Available online 12 February 2014

Keywords:
Thermoelectric cooling
Thermoelectric material
Modeling
Application

ABSTRACT

This study reviews the recent advances of thermoelectric materials, modeling approaches, and applications. Thermoelectric cooling systems have advantages over conventional cooling devices, including compact in size, light in weight, high reliability, no mechanical moving parts, no working fluid, being powered by direct current, and easily switching between cooling and heating modes. In this study, historical development of thermoelectric cooling has been briefly introduced first. Next, the development of thermoelectric materials has been given and the achievements in past decade have been summarized. To improve thermoelectric cooling system's performance, the modeling techniques have been described for both the thermoelement modeling and thermoelectric cooler (TEC) modeling including standard simplified energy equilibrium model, one-dimensional and three-dimensional models, and numerical compact model. Finally, the thermoelectric cooling applications have been reviewed in aspects of domestic refrigeration, electronic cooling, scientific application, and automobile air conditioning and seat temperature control, with summaries for the commercially available thermoelectric modules and thermoelectric refrigerators. It is expected that this study will be beneficial to thermoelectric cooling system design, simulation, and analysis.

1. Introduction

Thermoelectric cooling, commonly referred to as cooling technology using thermoelectric coolers (TECs), has advantages of high reliability, no mechanical moving parts, compact in size and light in weight, and no working fluid. In addition, it possesses advantage that it can be powered by direct current (DC) electric sources, such as photovoltaic (PV) cells, fuel cells and car DC electric sources. The main disadvantages of thermoelectric cooling are the high cost and low energy efficiency, which has restricted its application to cases where system cost and energy efficiency are less important than energy availability, system reliability and quiet operation environment. Though thermoelectric cooling effect was discovered in the 19th century, it hadn't come to rapid development until 1950s when the basic science of thermoelectric materials became well established [1].

Thermoelectric module is a solid-state energy converter that consists of a bunch of thermocouples wired electrically in series and thermally in parallel. A thermocouple is made of two different semiconducting thermoelements, which generate thermoelectric cooling effect (Peltier–Seebeck effect) when a voltage in appropriate direction applied through the connected junction. Thermoelectric module generally works with two heat sinks attached to its hot and cold sides in order to enhance heat transfer and system performance. For a specific module and fixed hot/cold side temperatures, there exists an optimum current for maximum

* Corresponding author. Tel.: +1 307 766 2017; fax: +1 307 766 2221.
E-mail address: gtan@uwyo.edu (G. Tan).

http://dx.doi.org/10.1016/j.applthermaleng.2014.01.074
1359-4311/Published by Elsevier Ltd.

Nomenclature

A	cross-sectional area, m^2
COP	coefficient of performance
C_p	heat capacity, J kg^{-1} K^{-1}
E	electric field, V m^{-1}
f	thermoelectric module packing fraction covered by thermoelement
h	convective heat transfer coefficient, W m^{-2} K^{-1}
I	electric current, A
j	electric current density, A m^{-2}
k	thermal conductivity, W m^{-1} K^{-1}
K	thermal conductance, W K^{-1}
l	thermoelementlength, m
N	number of thermocouples
P	electrical power supply, W
q	energy in thermoelement scale, W
Q	energy in thermoelectric module scale, W
R	electrical resistance, Ω
t	time, s
T	temperature, °C
x	length, m
X	slenderness ratio
ZT	dimensionless figure-of-merit

Greek symbols

α	Seebeck coefficient, V K^{-1}
β	ratio of the Thomson heat to the thermal conduction
ΔT	temperature difference between hot and cold sides, K
ε	emissivity
φ	ratio of temperature difference to the hot side temperature
θ	non-dimensional temperature
ξ	non-dimensional length
ρ	electrical resistivity, Ω m
ρ	density, kg m^{-3}
γ	combination heat transfer coefficient of radiation and convection in Eq. (8) W m^{-2} K^{-1}
γ	ratio of the Joule heating to the thermal conduction in Eq. (12)
σ	electrical conductivity, S m^{-1}
σ_b	Stefan–Boltzman constant, 5.67 × 10^{-8} W m^{-2} K^{-4}
τ	Thomson coefficient, V K^{-1}
ϕ	electric scalar potential, V

Subscripts

c	cold side
con	conduction
e	thermoelement
h	hot side
m	mean/average
max	maximum
n	n-type thermoelement
p	constant pressure
p	p-type thermoelement
∞	ambient

Overbar

	temperature independent value

coefficient of performance (COP) as shown in Eq. (1) [2]. Fig. 1 shows the cooling COP variation of a thermoelectric module under optimum current with fixed hot side temperature of 300 K.

$$(\mathrm{COP})_{c,\,max} = \frac{T_c}{T_h - T_c}\frac{\sqrt{1+ZT_m} - \frac{T_h}{T_c}}{\sqrt{1+ZT_m}+1} \tag{1}$$

where, ZT_m is the thermoelectric material figure-of-merit at average hot and cold side temperature T_m.

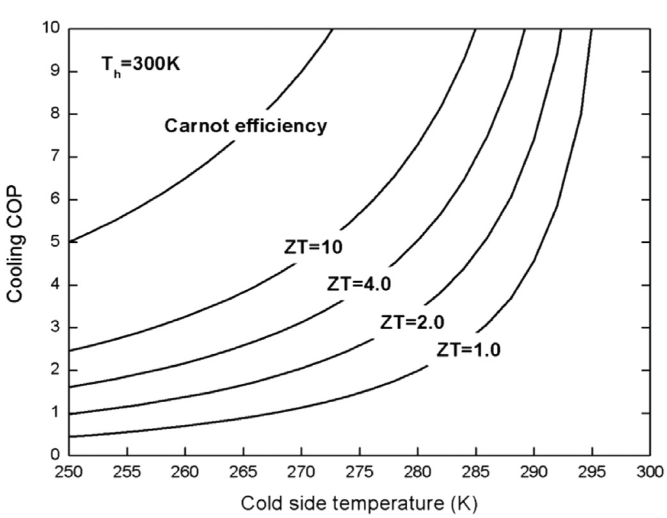

Fig. 1. Cooling COP of a thermoelectric module under optimum electrical current with fixed hot side temperature of 300 K.

Besides its applications in military, aerospace, industrial and scientific work, thermoelectric cooling is gradually getting more involvement into people's daily life. Thermoelectric cooling devices are widely used for electronic cooling such as PC-processors, portable food & beverage storages, temperature-control car seats and even thermoelectric air-conditioners. Scientific community has placed huge amount of efforts on thermoelectric cooling research.

There are good review papers on thermoelectric technologies and applications, including modeling and analysis of thermoelectric modules [3], solar-based thermoelectric technologies [4], cooling, heating, generating power, and waste heat recovery [5,6]. Riffat and Ma [2] presented a review of COP improving for thermoelectric cooling systems in 2004. Recent research provides two possible paths that may lead to significant progress in thermoelectric cooling [4]: 1) to improve the intrinsic efficiencies of thermoelectric materials, and 2) to improve thermoelectric cooling system's thermal design and optimization based on currently available thermoelectric modules. This review work focuses on the development of thermoelectric cooling in recent decade with particular attention on advances in materials, modeling and optimization approaches, and applications.

2. Development of thermoelectric materials

Reviews have summarized progress on thermoelectric materials [7–10], bulk thermoelectric materials [11,12], and low-dimensional thermoelectric materials [1,13–15].

As shown by the primary criterion of merit $ZT = \alpha^2\sigma T/k$, a good thermoelectric material should have high Seebeck coefficient, high electrical conductivity (or high power factor), and low thermal conductivity. However, since these three parameters are interrelated, following the Wiedemann–Franz law [16], researches have to

optimize these conflicting parameters to get the maximized *ZT*. To some extent, the ability to reduce material thermal conductivity, especially the lattice thermal conductivity, is critical to optimize the thermoelectric material's performance [1].

Conventional thermoelectric materials are bulk alloy materials such as Bi_2Te_3, PbTe, SiGe and $CoSb_3$, among which Bi_2Te_3 is the most commonly used one. They usually process a *ZT* value less than one. From 1960s to 1990s, achievement in increasing *ZT* was modest. After the mid-1990s, theoretical predications suggested that thermoelectric material efficiency could be greatly enhanced through nanostructural engineering [8]. Meanwhile, owing to the modern synthesis and characterization techniques, conventional bulk materials containing nanostructured constitutes have been explored and found so that high efficiencies could be achieved. Thus, in nowadays, the advances in *ZT* factor came from two primary approaches: 1) bulk samples containing nanoscale constitutes, and 2) nanoscale materials themselves.

Regard to the approach of bulk samples containing nanoscale constitutes, researchers have figured out that good thermoelectric materials are the so called "phonon-glass electron-crystal (PGEC)" material [8,11], where high mobility electrons are free to transport charge and heat but the phonons are disrupted at the atomic scale from transporting heat. Some primary bulk thermoelectric materials are skutterudites, clathrates and half-Heusler alloys, which are principally produced through doping method.

Low-dimensional materials, including 2D quantum wells, 1D quantum wires and 0D quantum dots, process the quantum confinement effect of the electron charge carriers which could enhance the Seebeck coefficient and thus the power factor. Furthermore, the numerous interfaces introduced will scatter phonons more effectively than electrons so that the thermal conductivity would be reduced more than the electrical conductivity [1].

Recently, Liu et al. [17] performed a liquid-like behavior of copper ions around a crystalline sublattice of Se in $Cu_{2-x}Se$ that results in an intrinsically very low lattice thermal conductivity which enables high *ZT* in this simple semiconductor. The results indicate a new strategy and direction for high-efficiency "phonon-liquid electron-crystal" thermoelectric materials by exploring systems where there exists a crystalline sublattice for electronic conduction surrounded by liquid-like ions.

The best commercial thermoelectric materials currently have *ZT* values around 1.0. The highest *ZT* value in research is about 3, reported by Harman in 2005 [18]. Other best reported thermoelectric materials have figure-of-merit values of 1.2–2.2 at temperature range of 600–800 K, as shown in Table 1. It is estimated that thermoelectric coolers with *ZT* value of 1.0 operate at only 10% of Carnot efficiency. Some 30% of Carnot efficiency (comparable to home refrigeration) could be reached by a device with a *ZT* value of 4. However, increasing *ZT* to 4 has remained a formidable challenge [19]. Bell [5] also mentioned that if the average *ZT* reaches 2, domestic and commercial solid-state heating, ventilating and air-cooling systems using thermoelectric material would become practical.

Table 1
A summary of high figure-of-merit thermoelectric materials reported in this decade.

Material	Type	*ZT* value	Temperature	Ref.
Bi-doped PbSeTe/PbTe (QDSL)	n-type	3	550 K	[18]
$In_{0.2}Ce_{0.15}Co_4Sb_{12}$ Skutterudite	n-type	1.43	800 K	[20]
$Pb_{0.25}Sn_{0.25}Ge_{0.5}Te$	p-type	~0.95	670 K	[21]
$(Bi_{0.25}Sb_{0.75})_2Te_3$	p-type	1.27	298 K	[22]
$Bi_2(Te_{0.94}Se_{0.06})_3$	n-type	1.25	298 K	[22]
$K_{0.95}Pb_{20}Sb_{1.2}Te_{22}$	n-type	~1.6	750 K	[23]
PbTe–SrTe	p-type	1.7	~800 K	[24]
Binary crystalline $In_4Se_{3-\delta}$	n-type	1.48	~705 K	[25]
$AgPb_mSbTe_{2+m}$	n-type	~2.2	800 K	[26]

3. Modeling approaches for thermoelectric cooling

3.1. Thermoelement modeling

The basic unit of the thermoelectric cooler is the n-type and p-type thermoelements. A bottom-up modeling approach is to construct the model at element level with the assumption that both types of thermoelements are exactly the same except opposite direction of the Peltier–Seebeck effect.

3.1.1. Standard simplified energy equilibrium model

The standard simplified energy equilibrium model for thermoelement is based on the balance of heat transfer and thermoelectric effects. Assumptions have been made that 1) thermoelectric material properties are temperature independent, 2) and half of the Joule heat goes to the hot side while the other half goes to cold side. Energy absorbed at the thermoelement's cold side (q_c) can be then described as the follows [2]:

$$q_c = q_{e,c} - 0.5q_{e,J} - q_{e.con} = \overline{\alpha}_{e,c}IT_c - 0.5I^2\overline{R}_e - \overline{K}_e(T_h - T_c) \quad (2)$$

where, $q_{e,c}$ is the Peltier effect generated cooling at the thermoelement cold side, $q_{e,J}$ is the Joule heat due to current flowing through and $q_{e,con}$ is the heat conduction from hot side to cold side. The thermoelement properties $\overline{R}_e$ and $\overline{K}_e$ are remained constant and evaluated from the mean of T_h and T_c.

The input electrical power (P_e) is given by:

$$P_e = I^2\overline{R}_e + \overline{\alpha}_e I(T_h - T_c) \quad (3)$$

For more accurate modeling, the neglected Thomson effect also has to be taken into consideration. The general form of Thomson coefficient is defined as in Eq. (4) [27,28]:

$$\tau = T\left(\frac{\partial \alpha_e}{\partial T}\right)_p \quad (4)$$

The improved simplified model is shown below in Eqs. (5) and (6) and it gives remarkable improvement compared to the standard simplified model above in Eqs. (2) and (3) [29].

$$q_c = \alpha_{e,c}IT_c - 0.5I^2\overline{R}_e - \overline{K}_e(T_h - T_c) + 0.5\overline{\tau}I(T_h - T_c) \quad (5)$$

$$P_e = (\alpha_{e,h}T_h - \alpha_{e,c}T_c)I + I^2\overline{R}_e - \overline{\tau}I(T_h - T_c) \quad (6)$$

Thomson coefficient here can be derived from Eq. (4) and shown below in Eq. (7):

$$\overline{\tau} = T_m\frac{\alpha_{e,h} - \alpha_{e,c}}{T_h - T_c} \quad (7)$$

In this case, although $\overline{K}_e$ and $\overline{R}_e$ are still temperature independent values and generally evaluated by mean temperature T_m, Seebeck coefficient $\overline{\alpha}_e$ will be evaluated from hot and cold side temperatures separately for $\alpha_{e,c}$ and $\alpha_{e,h}$. $\overline{\tau}$ is evaluated from hot/cold side temperatures and Seebeck coefficients.

3.1.2. One-dimensional thermoelement modeling

The assumption of temperature independent thermoelectric material parameters in simplified energy equilibrium modeling approach could result in up to 10% error comparing to the true values [30].

Temperature dependent parameters bring in two complications [27,31]. One is the temperature dependent Thomson effect. The other is that Thomson effect, Joule heat and heat conduction have to be considered together since the temperature distribution is no longer linear through the thermoelement. More general one-dimensional transient model thus has been proposed and studied by several researchers [27,31,32], of which the governing equation is as follows:

$$\rho C_p \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(k(T)\frac{\partial T(x,t)}{\partial x}\right) + \frac{1}{\sigma(T)}j^2 - j\tau\frac{\partial T(x,t)}{\partial x} - \gamma A_e(T(x,t) - T_\infty) \quad (8)$$

The one-dimensional thermoelement model solves detailed temperature distribution along thermoelement length. In Eq. (8), terms on the right side represent, respectively, conduction heat transfer rate, Joule heat generation rate, the Thomson effect, and the combined radiation and convection heat transfer rate with ambient ($\gamma = 4\varepsilon\sigma_b T_\infty^3 + h$). In general, the last term may be negligible compared to the others.

During this modeling process, the electrical current density ($j = I/A_e$) is treated as uniform and thus there is no need to solve the electric potential equation. However, in fact, temperature field and electric potential field are coupled in the thermoelement [33]. If more precise numerical result is required, the temperature equation and electric potential equation should be coupled [34].

$$\frac{\partial}{\partial x}\left(\sigma\left(\frac{\partial \phi}{\partial x} - \alpha\frac{\partial T}{\partial x}\right)\right) = 0 \quad (9)$$

$$E = -\frac{\partial \phi}{\partial x} + \alpha\frac{\partial T}{\partial x} \quad (10)$$

$$j = \sigma E \quad (11)$$

Eq. (9) is the one-dimensional electric potential field equation. Once the electric potential (ϕ) is obtained, the electric field (E) and electric current density (j) can be calculated.

In numerical modeling, the non-dimensional parameters offer convenience to generalize and simplify the shape of the governing equations. For instance, Huang et al. [27] and Lee [35] introduced non-dimensional analysis and used dimensionless governing equations in order to get the one-dimensional exact solutions. The non-dimensional equation given by Lee [35] is

$$\frac{d^2\theta}{d\xi^2} - \beta((\theta - 1)\varphi + 1)\frac{d\theta}{d\xi} + \gamma = 0 \quad (12)$$

where $\theta = (T - T_c)/(T_h - T_c)$, $\xi = x/l$, β is the ratio of the Thomson heat to the thermal conduction, γ is the ratio of the Joule heating to the thermal conduction, and φ is the ratio of temperature difference to the high junction temperature as shown in Eqs. (13)–(15).

$$\beta = \frac{IT_h\frac{d\alpha}{dT}\Delta T}{A_e k\frac{\Delta T}{l}} \quad (13)$$

$$\gamma = \frac{I^2 R}{A_e k\frac{\Delta T}{l}} \quad (14)$$

$$\varphi = \frac{\Delta T}{T_h} \quad (15)$$

Fraisse et al. [29] presented a comparison study for four different modeling approaches applied for thermoelement, including standard simplified models, analytical models, model based on electrical analogy between heat transfer and electricity [36], and numerical models based on the finite element method (FEM). Selection between different models is highly depending on the modeling goal aimed as a tradeoff exists between the modeling accuracy and the computational efforts.

3.1.3. Three-dimensional thermoelement modeling

Three-dimensional modeling [33,34,37,38] captures temperature distribution both along and across the thermoelement, thus, it performs better than one-dimensional modeling. However, more computational effort is required. Governing equation for three-dimensional modeling can be obtained by simply extending Eq. (8) to three-dimensional. To reduce computational cost, thermoelectric material properties are sometimes treated as constant. Cheng et al. [37] developed a transient three-dimensional constant property model for a single thermocouple (two thermoelements) with mesh grid 31 × 31 × 46 and close agreement was obtained between the numerical and experimental data. Wang et al. [33] reported a general three-dimensional temperature-dependent property thermoelement model with coupling of the temperature and electric potential field. Results showed that temperature-dependent property and heat losses to the ambient have significant effects on cooling capacity and COP.

In one-dimensional and three-dimensional modeling, usually unsteady nonlinear second-order partial differential equations such as Eq. (8) need to be solved. Numerical methods are frequently employed and thus numerical analysis software tool such as MATHEMATICA [31], COMSOL Multiphysics [39], ANSYS [32,35,40,41] has been applied in research works.

3.2. Thermoelectric cooler (TEC) modeling

3.2.1. Simplified energy equilibrium model

The simplified energy equilibrium model, have similar shape as Eqs. (2) and (3) but applied to a TEC module, has been used and validated by many researchers [2,31,42–49] as shown below:

$$Q_c = \overline{\alpha} I T_c - \overline{K}(T_h - T_c) - 0.5\overline{R}I^2 \quad (16)$$

$$P = I^2\overline{R} + \overline{\alpha}I(T_h - T_c) \quad (17)$$

where, $\overline{\alpha}$, $\overline{R}$ and $\overline{K}$ are thermoelectric module Seebeck coefficient, electrical resistance and thermal conductance. For this model, once these temperature independent module parameters are obtained, module cooling power output and COP can be calculated. However, for commercially available thermoelectric modules, the manufacturer may not provide the thermoelectric module material parameters. Palacios et al. [50] proposed an analytical procedure to obtain those internal parameters from performance curves. Chen and Snyder [51] also developed the following equations which using operation parameters Q_{max}, ΔT_{max}, and I_{max} to obtain thermoelement Seebeck coefficient $\overline{\alpha}_e$, electrical resistivity $\overline{\rho}$ and thermal conductivity $\overline{k}$.

$$\overline{\alpha}_e = \frac{Q_{max}(T_h - \Delta T_{max})}{N T_h^2 I_{max}} \quad (18)$$

$$\overline{\rho} = \frac{Af(T_h - \Delta T_{max})^2}{2T_h^2 l}\frac{Q_{max}}{N^2 I_{max}^2} \quad (19)$$

$$\overline{k} = \frac{l(T_h - \Delta T_{max})^2}{Af T_h^2}\frac{Q_{max}}{\Delta T_{max}} \quad (20)$$

Thermoelectric module $\overline{\alpha}$, $\overline{R}$ and $\overline{K}$ are then calculated from the material electrical resistivity and thermal conductivity respectively in Eqs. (21)–(23).

$$\overline{\alpha} = N\overline{\alpha}_e \tag{21}$$

$$\overline{R} = \frac{N^2 l\overline{\rho}}{Af} \tag{22}$$

$$\overline{K} = \overline{k}\frac{Af}{l} \tag{23}$$

Alternatively, since thermoelectric cooler consists of a bunch of thermoelements, thus the other way to obtain thermoelectric module cooling capacity (Q_c) and electrical power input (P) is to simply use thermoelement cooling capacity (q_c) and thermoelement electrical power input (P_e) in Eqs. (2) and (3) multiply with thermoelement numbers [52].

3.2.2. Numerical compact modeling for thermoelectric cooler

Since thermoelectric cooler consists of thermoelements, thus for thermoelectric cooler modeling, it is reasonable to numerically model every thermoelements in a thermoelectric cooler. Chen et al. [40] presented a three-dimensional numerical study for miniature thermoelectric cooler consists of 8, 20 and 40 pairs of thermocouples. Seebeck coefficient was treated as temperature dependent while thermal and electrical conductivity were kept constant. The prediction indicates that cooling power and COP of the module are increasing notably when thermocouples inside a module are scaled down. However, this approach is very computationally expensive and complicated, because the mesh grids have to be extremely small in size to modeling each p-type and n-type thermoelement. Furthermore, thermal and electrical contact resistance will make the modeling process even more complicated [30].

Instead of modeling each thermoelement individually, modeling the thermoelectric cooler as a single bulk is a much easier approach. This kind of so-called compact models can handle the multiscale issue using fine mesh and coarse mesh at different regions respectively. Chen and Snyder [51] developed a compact modeling approach for thermoelectric coolers. It is demonstrated that with the results almost as accurate as the physical model (numerical study includes all coupled thermoelectric as well as components that provide losses and other parasitic effects), a significant amount of grid has been reduced and computational speed is roughly 100 times faster. The critical technique for compact modeling is to determine effective Seebeck coefficient, thermal and electrical conductivity for the compact thermoelectric cooler.

4. Strategies for improving the cooling system performance

In the design of a thermoelectric cooling system, one has to take into account both the system cooling power output and cooling COP with consideration of both the thermoelectric module performance and the heat sink design. Therefore, in fact, thermoelectric cooling system design is a compromise between the cooling capacity and COP.

There are three methods leading the enhancement of thermoelectric cooling system performance. The first one is through thermoelectric module design and optimization, such as the thermoelement length [36,38,53–55], number of thermocouples [38,56–58], thermoelement length to cross-sectional area ratio [41,56,59,60], slenderness ratio ($X = (A_p/l_p)/(A_n/l_n)$) [61] and thermoelement with non-constant cross section area [62]. The second approach relates to cooling system thermal design and optimization [63], which includes investigation of heat sinks' geometry [42,64–66], allocation of the heat transfer area and heat transfer coefficients of hot and cold side heat sinks [44,67–69], thermal and electrical contact resistances and interface layer analysis [70–72], more effective heat sinks (i.e. heat sink integrated with thermosyphon and phase change material) [74,75,88]. The third approach relates to the thermoelectric cooling system working condition (i.e. electric current input [37,76,77]), heat sink coolant, and coolant's mass flow rate [49,78].

A variety of system optimization methods have been adopted. Cheng and Lin [53] used genetic algorithms to optimize thermoelement physical dimensions (length, cross-sectional area and number of thermoelements). Lineykin and Yaakov [79] provided a user friendly and intuitive graphical approach to the design of thermoelectric cooling system. Chakraborty et al. [80] presented the temperature–entropy analysis to demonstrate the cooling cycle of a thermoelement. Zhang [76] introduced a general straightforward approach, instead of the commonly used iterative procedure, to optimize thermoelectric coolers. Dimensionless analysis method, with the advantage of reducing optimum design parameters, has been performed in open literature by several authors. Wang et al. [67] introduced the dimensionless entropy generation number based on thermal conductance to evaluate the external irreversibility in the thermoelectric cooling system, which takes both first and second law of thermodynamics into consideration. Lee [56] developed new dimensionless groups to represent important parameters of the thermoelectric devices such as the thermal conduction ratio, the convection conduction ratio, and the load resistance ratio.

Based on research works discussed in this section, summaries can be concluded as below:

- The simplified energy equilibrium model for thermoelectric cooler can satisfy many thermoelectric cooling applications such as electronic devices cooling and air-conditioning [42–49].
- If the thermoelectric modules are employed with time-varying temperature distribution and cooling power output, either 1D or 3D transient modeling is needed to better capture the system performance. In 3D model, thermoelectric thermophysical properties are usually treated as independent of temperature for simplification.
- Although p-type and n-type thermoelements have different values of Seebeck coefficient, electrical conductivity, and thermal conductivity in one thermoelectric module, to some extent, these differences are negligible in numerical study. Therefore, only one set of Seebeck coefficient, electrical and thermal conductivity will be used in simulation.
- Modeling temperature change in all thermoelements to capture the module performance is very complicated and time consuming. Energy equilibrium model or compact model can be applied to simplify the numerical study process, especially for system modeling including heat sinks in hot and cold sides.
- Thomson effect comes with the temperature dependent Seebeck coefficient. Positive Thomson coefficient improves thermoelectric cooling performance by 5–7% [40], while negative Thomson coefficient reduces cooling performance [35]. However, for commercially available thermoelectric coolers, Thomson effect is often small and negligible. Snyder et al. [81] developed the concept 'Thomson cooler' and predicted that with equivalent ZT, higher hot/cold side temperature difference can be achieved than the traditional Peltier cooler.
- Both COP and cooling capacity are dependent on thermoelement length, and this dependence becomes increasingly significant with a decrease in thermoelement length [2]. In case other parameters (such as the cross section area) of

thermoelement are constant, then in general, longer thermoelement length helps achieve a greater COP, while shorter thermoelement length results in larger cooling capacity. Most commercially available thermoelectric modules have thermoelement length range from 1.0×10^{-3} m to 2.5×10^{-3} m.

- Cooling power density increases with decreasing the ratio of thermoelement length to cross-sectional area.
- Thermal and electrical contact resistances, especially thermal contact resistance at the thermoelement interface layer, are critical for both thermoelectric cooling capacity and COP. The increase in *ZT* of a thermoelectric material doesn't necessarily mean increase in *ZT* of a thermoelement as long as the presence of the interface layer [71].
- The efficiency of the heat sinks at hot and cold side greatly influences the cooling COP. Air cooled heat sink (forced convection with fan, example thermal resistances of 0.54–0.66 K/W [82] and 0.5 K/W [49]), water cooled heat sink (example thermal resistance of 0.108 K/W [45]) and heat sink integrated with heat pipe (example thermal resistance of 0.11 K/W [73]) are frequently employed techniques. Research found heat pipe doesn't benefit too much for heat dissipation as heat pipe has to release heat to either air or water finally. Recently, heat sinks with nanofluid have shown potential to achieve lower thermal resistance [83,84]. In addition, cooling technologies based on heat removal from the heat sinks using synthetic jet [85] or microchannel [86], either single-phase or two-phase flow, are noticeable.
- Heat sink performance at the hot side is more important than heat sink at the cold side because the heat flux density at hot side is higher. Allocation of the heat transfer area or heat transfer coefficients between hot and cold sides is particularly important. For a thermoelectric module with given cooling capacity, there exists an optimum allocation ratio to achieve maximum COP. Some typical allocation ratio is around 0.36–0.47 [44,68].

Table 2
Summary of commercially available thermoelectric modules from published literature.

Module type	Company	Q_{max} (W)	ΔT_{max} (°C)	Dimensions (mm)	Ref.
CP1.4-127-045	Melcor Corp.[a]	72[b]	75[b]	40 × 40 × 3.8	[34]
CP1.4-127-045L	Melcor Corp.	72	65	40 × 40 × 3.3	[105]
CP1.4-127-06L	Melcor Corp.	51.4	67	40 × 40 × 3.8	[49,67,96]
CP1.4-7-06L	Melcor Corp.	2.8	68	10 × 10 × 3.8	[106]
CP2-127-06	Melcor Corp.	120	68	62 × 62 × 4.6	[76]
CP2-127-06L	Melcor Corp.	120	67	62 × 62 × 4.6	[47,68,83,87]
HT8-12-40	Melcor Corp.	72	67	40 × 40 × 3.5	[76]
PT4-12-40	Melcor Corp.	32	67	40 × 40 × 4.1	[105]
TEC1-12706	HB Corp.	50	66	40 × 40 × 3.8	[46,107]
TEC1-12708	HB Corp.	71	66	40 × 40 × 3.5	[108,28]
TEC1-6308	HB Corp.	37.4	67	40 × 20 × 3.8	[109]
6L	Marlow Ind.	50	66	40 × 40 × 3.9	[75,88]
DT12-4	Marlow Ind.	36	66	30 × 30 × 3.3	[51]
UT8-12-40-RTV	Ultra TEC Series	72	–	–	[103]
TB-127-1.4-1.2	Kryotherm Corp.	75	70	40 × 40 × 3.5	[4]
TB-127-1.4-1.5	Kryotherm Corp.	60	70	40 × 40 × 3.9	[79]
TB-199-2.0-0.9	Kryotherm Corp.	310	69	62 × 62 × 3.2	[110]
TECA 980-127	TECA Corp.	83.2	72	15.7 × 15.7 × 1.3	[110]
9500/127/085B	Ferrotec Corp.	80	72	40 × 40 × 4	[111]
HM3930	Acetec Co.	16.7	69	30 × 30 × 4.7	[101]
CP10-127-05	Laird Tech.	34.3	67	30 × 30 × 3.2	[35]

[a] Melcor Corporation has been acquired by the Laird Group PLC ("Laird") and its products have adopted the name of the new company [112].
[b] Q_{max} and ΔT_{max} are evaluated by manufacturers at hot side temperature 297 K or 300 K.

- For given hot and cold sides fluid temperatures, there exists an optimum cooling capacity leading to maximum COP [56].
- Dimensionless analysis is a powerful tool to evaluate the performance of thermoelectric cooling system. New dimensionless parameters, such as dimensionless entropy generation number [67], dimensionless thermal conductance ratio and dimensionless convection ratio [56] have been defined.
- Precise manufacturing technique is critical to provide high quality thermoelectric modules, and precise manufacturing technique requires accurate determination of module parameters [2].

5. Thermoelectric cooling applications

Due to low COP, thermoelectric cooling has been restricted to niche applications, such as space missions, scientific and medical equipment, where COP is not as important as energy availability, reliability and quiet operation environment. However, as technology advanced, more and more new applications are emerging.

Current thermoelectric cooling applications can be categorized into five application areas. Firstly, in the civil market, thermoelectric cooling devices are used for cooling small enclosures, such as domestic and portable refrigerator, portable icebox, beverage can cooler and picnic basket [73,87–92]. Secondly, they have also been applied to medical applications [93], laboratory and scientific equipment cooling for laser diode or integrated circuit chip [94]. Thirdly, thermoelectric cooling devices have attracted great attention for heat dissipation in electronic devices cooling and industrial temperature control [42–45,68,82,95–99]. Moreover, applications can be found in automobile industry, such as automobile mini-refrigerators, thermoelectric cooler/heaters in car seats [3,100,101] and automobile air-conditioning applications [74,102]. At last, some researchers are in progress making thermoelectric domestic air-conditioning systems [46,103,104] in hoping they can be competitive with their vapor-compression counterparts. Table 2 summarizes commercially available thermoelectric modules from the published literature (see Table 3).

5.1. Thermoelectric refrigeration

Generally, there are two types of thermoelectric refrigeration devices: domestic and portable refrigerators. The major difference between these two is the availability of electrical power. Both domestic [73,87,88] and portable [89–91] refrigerators have been extensively studied. Although the thermodynamic efficiency of thermoelectric cooler is only 1% compared to 14% of Stirling and reciprocating vapor compression refrigeration systems [113], thermoelectric refrigerators offer advantages such as a more ecological system, more silent and robust and more precise in temperature control [92]. Thermoelectric refrigerators can be built into a limited space unit. Portable thermoelectric coolers have promising outdoor use, either using battery or powering by solar PV panels.

In general, the COP for both domestic and portable thermoelectric refrigerators is usually less than 0.5 when operating at an inside/outside temperature difference of 20–25 °C. Min and Rowe [87] conducted experimental evaluation to prototype thermoelectric domestic-refrigerators. The COP was found 0.3–0.5 for a typical operating temperature at 5 °C with ambient at 25 °C. Results also show that its COP is possibly enhanced through improvements in module contact resistances, thermal interfaces and the effectiveness of heat exchangers. Dai et al. [89,91] investigated a portable thermoelectric refrigerator driven by solar cells. Experiment results show that thermoelectric cooling can maintain temperature in the

Table 3
Summary of thermoelectric refrigerators reported in literature.

Dimension (m) or volume (m^3)	ΔT (°C) [a]	COP	Cooling capacity (W)	Heat sink techniques	Ref.
0.23 × 0.18 × 0.32	22	0.16	15.3	Finned heat sink and fan at the hot side	[90]
0.115	~20	0.3–0.5	50–100	Finned heat sink and fan in the cold side, liquid-heat exchanger at hot side	[87]
–	~20	0.23	12	Finned heat sink in the hot side	[89]
0.225	~10	0.393	19.4	Apply phase change thermosyphon system in both hot and cold sides	[88]
0.055	23.9	0.56–0.64	~30	Finned heat sink and fan at both hot and cold sides	[92]
0.25 × 0.25 × 0.35	–	0.22	9	Finned heat sink at the cold side, finned heat sink and fan at the hot side	[116]
0.056	19.8	~0.2	12.5	Finned heat sink and fan at both hot and cold sides	[113]

[a] ΔT is the inside/outside temperature difference of the refrigerators.

refrigerator at 5–10 °C with a COP of 0.23. Sabah et al. [90] experimentally investigated a portable solar thermoelectric refrigerator.

Usually, the inner temperature of a vapor compression refrigerator tends to have an oscillatory pattern due to the on/off cycles of the compressor, and the temperature fluctuation may be several degrees [114]. This effect is harmful to the conservation of food and other goods. Astrain et al. [115] developed a thermoelectric and vapor compression hybrid refrigerator which could maintain the temperature oscillation less than 0.4 °C.

5.2. Electronic cooling applications

Electronic devices like PC processors generate a huge amount of heat during operation which poses great thermal management challenge because reliable operation temperature for electronic devices has to be maintained. In most cases, the maximum electronic device junction temperature needs to be held less than 85 °C for reliable operation [42,77]. The maximum heat flow from a high performance electronic package can be about 200 W and is still constantly increasing [43]. Conventional passive cooling technologies using air or water as working fluid, such as the micro-channel sink, can't fully meet the heat dissipation requirement and active cooling methods should be applied. Due to the limited installation space in electronic packages, conventional bulk cooling systems are too big. Thermoelectric coolers combined with air cooling or liquid cooling approaches at the hot side show great potential because of their small size, high reliability and no noise. Phelan et al. [97] reviewed current and future miniature refrigeration cooling technologies for high power microelectronics and concluded that only thermoelectric coolers are now commercially available in small sizes.

The performance of the thermoelectric cooler is much more sensitive to the thermal resistance between the cooler and the ambient air than the thermal resistance between the chip and the cooler. Naphon and Wiriyasart [65] compared liquid cooling in the mini-rectangular fin heat sink with and without thermoelectric cooler for CPU and found that thermoelectric cooler plays a key effect factor. When combined with air cooling device for the hot side, thermoelectric coolers perform better at a lower thermal load, for example, 20 W [82]. Instead, for a high thermal load, thermoelectric air cooling device may be not as effective as the air cooling heat sink. However, if combined with water cooling device in electronic equipment, thermoelectric coolers usually perform better in a relatively higher thermal load, e.g. 57 W [45]. Chein and Huang [42] conducted a theoretical investigation on thermoelectric cooler application in electronic cooling for both air and liquid cooling approaches. The highest cooling capacity obtained in their study was 207 W. Nanofluids have shown potential for the liquid cooling approach as nanofluids offer a better choice than water and can further increase cooling power output [83,84].

5.3. Automobile cooling applications

Most of automobile air-conditioning systems currently use R-134a as refrigerant. R-134a does not have ozone-depleting effect but still faces the global warming effect. Leakage problem of the refrigerant in automobiles is more substantial than that in stationary air conditioners. Thermoelectric coolers have advantages of compact size, no moving parts and working fluid, compatible with automobile electrical system voltage, and easily switching between heating and cooling modes. Therefore, thermoelectric cooler appears to be especially favorable for automotive application. Yang and Stabler [117] presented a review on automotive applications of thermoelectric materials. Luo et al. [74] presented a novel thermoelectric air-conditioner for a truck cab. COP of the cooling system was tested to be 0.4–0.8 under ambient temperature from 46 to 30 °C. They also found that the cooling performance can be further improved by optimizing system design and manufacture craft.

Besides the automobile air-conditioning system, researchers also utilized thermoelectric device to control car-seat temperature. Hyeung-Sik et al. [100] developed a temperature-controlled car-seat system utilizing thermoelectric device to either cooling down or heating up the car-seat. The control scheme was implemented by using a one-chip microprocessor, and the performance of device validated by experiments. Gentherm (former Amerigon) company developed their principal thermoelectric product, the Climate Control Seat (CCS), which delivers a thermal comfort to automotive and truck drivers [101]. A large cooling device market in automotive industry has already opened for thermoelectric cooling devices and will continue expanding in the next decades.

5.4. Thermoelectric air-conditioning applications

Researchers are in progress making thermoelectric domestic air-conditioning systems in hoping they can be competitive with their vapor-compression counterparts. Riffat and Qiu [118] compared performances of thermoelectric and conventional vapor compression air-conditioners. Results show that the actual COPs of vapor compression and thermoelectric air-conditioners are in the range of 2.6–3.0 and 0.38–0.45, respectively. However, thermoelectric air conditioners have several advantageous features compared to their vapor-compression counterparts. For example, they can be built into a planar structure which can be easily handled on walls and they offer a quiet operation environment especially suitable for household use.

Cosnier et al. [47] presented an experimental and numerical study of a thermoelectric air-cooling and air-heating system. They have reached a cooling power of 50 W per module, with a COP between 1.5 and 2, by supplying an electrical intensity of 4 A and maintaining 5 °C temperature difference between the hot and cold sides. Cheng et al. [104] designed a solar-driven thermoelectric

cooling module with a waste heat regeneration unit for green building applications. Results show that the system is able to produce 16.2 °C temperature difference between the ambient environment and inside the model house. However, the thermoelectric device cooling COP is relatively low, from −0.2 to 1.2 in this study. Gillott et al. [103] investigated thermoelectric cooling devices for small-scale space's conditioning application in buildings. A thermoelectric cooling unit was assembled and generated up to 220 W cooling capacity with a maximum COP of 0.46 under the input electrical current of 4.8 A for each module.

Arenas et al. [119] and Vázquez et al. [120] introduced active thermal window (ATW) and transparent active thermoelectric wall (PTA) for room cooling application in case conventional air conditioning system is difficult to install, such as for old historic building restoration. The thermoelements embedded in window glass will transfer heat through the glass in order to cool the room. A full-size prototype ATW was installed in a window frame (100 × 100 cm) and was able to generate up to 150 W of cooling power while glass transparency decreased in less than 20%. Their work has been patented in Spain [121].

Most of thermoelectric cooling devices directly cool down indoor air. Shen et al. [46] investigated a novel thermoelectric radiant air-conditioning system (TE-RAC). The system employs thermoelectric modules as radiant panels for indoor cooling, as well as for space heating by easily reversing the input current. Based on the analysis of a commercial thermoelectric module, TEC1-12706 with a *ZT* value of 0.765, they have obtained a maximum cooling COP of 1.77 when applying an electric current of 1.2 A and maintaining cold side temperature at 20 °C.

5.5. Other thermoelectric cooling applications

Besides the applications discussed above, thermoelectric cooling has been applied to other occasions, such as generating fresh water [107,108,110], active building envelope system [105,106], photovoltaic-thermoelectric (PV-TE) hybrid module [104,122,123], and thermal management for high-power LEDs [109,111].

Photovoltaic (PV) modules suffer from elevated outdoor temperature which results in dropping efficiency. Researchers proposed using the thermal waste by attaching thermoelectric modules to the back of PV to form a photovoltaic-thermoelectric (PV-TE) hybrid module. Additional electricity can be generated through the thermoelectric module. Sark [122] found that this approach may lead to efficiency enhancement by up to 23% for roof integrated PV-TE modules using commercial available thermoelectric materials, while the annual energy yield would increase by 11%–14.7%. This application technically belongs to thermoelectric power generation. However, the thermoelectric module introduced here helps cool down the PV panels. Dessel and Foubert [106] investigated active thermal insulator using thermoelectric modules integrated into a double pane glazing system, which aims to using solar energy to compensate the passive heat losses or gains in building envelopes. This effect has been accomplished by integrating photovoltaic (PV) and thermoelectric systems into a wall assembly. A portable active solar still using thermoelectric cooling has been studied by Esfahani et al. [107] in order to enhance water productivity.

About thermoelectric cooling applications, following general summaries can be drawn from literature:

- Besides the cooling application in areas such as domestic and portable refrigeration, heat dissipation and temperature control in electronic systems, medical and scientific applications, automobile heating and cooling, thermoelectric cooling also show potential in other areas such as domestic air-conditioning, integrating with solar PV, and solar still.
- Cooling COP of thermoelectric refrigerators are generally in the range 0.16–0.64 with a temperature difference around 20 °C, depending on the performance of hot and cold side heat sinks.
- The major advantages of thermoelectric devices applied to electronic cooling are the compact size and large cooling density, which meets requirement of a single-chip package with heat dissipation rate of 250 W or even higher.
- The DC power need of thermoelectric device matches well with the automotive electric power supply. Integrating with automotive has been the best commercialized application. Large amount of car seats and refrigerators are already available in the market, while thermoelectric car air-conditioning system is still in progress.
- Development of domestic thermoelectric air-conditioning is very challenging because its vapor-compression counterparts have high economic effectiveness. However, thermoelectric air-conditioning may gain advantage when a big breakthrough for thermoelectric material has been achieved.
- There are two ways to combine thermoelectric modules and solar PV panels: 1) PV panels provide direct current for thermoelectric cooling; 2) thermoelectric modules are attached to the back side of PV panels to decrease panel temperature, thus increase PV panel efficiency, and gain extra electric power from thermoelectric modules.
- Multistage cooling (usually two to six stages) can achieve hot and cold side temperature difference as high as 130–150 K, which is the thermoelectric cascaded module, by taking the advantage of different thermoelectric materials' different working temperatures. Multistage cooling can achieve low cold side temperature and is appropriate for cryogenic applications.

6. Summary

This paper reviews the development of thermoelectric cooling in the recent decade from aspects of advances in materials, the modeling approaches, and applications.

The advances in thermoelectric material make it possible to significantly improve *ZT* factor through nanotechnology. Two primary approaches are bulk samples containing nanoscale constitutes and low dimensional materials. New thermoelectric materials with larger *ZT* factor values may intriguer a breakthrough in various application areas for thermoelectric devices.

Different thermoelectric modeling approaches have been summarized in this review. The simplified models reduce computational efforts at the cost of giving up some level of modeling accuracy. Model selection is highly dependent on the modeling goal aimed. There are three pathways that may lead to the enhancement of thermoelectric cooling devices' performance: 1) through the thermoelectric module design and optimization, 2) through cooling system thermal design and optimization, 3) through thermoelectric cooling system's working condition improvement.

Typical applications of thermoelectric cooling have been summarized in five categories, including domestic refrigeration, electronic cooling, scientific, and automobile applications. However, thermoelectric cooling applications are not limited to these areas. More applications are emerging when high quality thermoelectric materials have been developed and the thermoelectric cooling devices are approaching higher performance efficiency.

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